DESIGN AND DEVELOPMENT OF NANOSTRUCTURED Cu_2XSnS_4 (X= Zn, Co and Ni) QUATERNARY THIN FILM ELECTRODES FOR ADVANCED ENERGY STORAGE SYSTEMS

A SYNOPSIS

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1. INTRODUCTION

The global energy consumption will continue to increase over the next few decades, due to the increase in world population and quality of life. The rapid decline in fossil fuels and the increase in green-house gas emissions have made people seriously think of alternatives to non-conventional energy sources. In turn, the increase in social development and human health will be detrimental global warming due to over-consumption of conventional fossil fuels such as coal, oil and natural gas. To overcome these problems, the world is moving towards the development of clean and sustainable energy sources to replace these fossil fuels. With this approach, a greater amount of clean and sustainable energy can be generated by converting natural energy such as wind, wave and solar energy. The development of energy storage devices is crucial for storing harvested energy for wider applications [1, 2]. Electrochemical energy storage devices such as batteries, supercapacitors and fuel cells are based on the principle of conversion from chemical to electrical energy and are reliable alternatives due to their unique features. Electrochemical energy storage devices are used for a wide range of applications in consumer electronics such as mobile phones, iPods, laptops, digital cameras, emergency doors, military and aerospace and hybrid vehicles. Light-weight, flexible, high-performance and low-cost energy storage devices are essential to meet future energy needs. This situation has encouraged researchers to explore high energy storage technologies [3-5] such as sodium-ion batteries, lithium-ion batteries and supercapacitors (SCs), etc.

The energy and power storage properties in the energy storage systems critically affects the commercial viability of emerging technologies. For example, the realization of electric vehicles depends on the presence of energy storage systems with significantly improves energy and power density, durability and reduced cost. Although great efforts have been made to develop high-performance Li-ion batteries [6], poor electrical efficiency and high maintenance cost have kept them away from various applications. Recently, supercapacitors have attracted a lot of attention because of their high charge discharge rate, long cycle stability, outstanding power density and no short circuit concern [7]. Therefore, they can provide more power due to their efficiency releases energy much more easily from the surface or sub-surface layer than from the aggregate. As the charging-discharging occurs on the surface, it does not trigger a rigid structural change in electro active materials make supercapacitors better cycling capabilities. Due to these unique features,

supercapacitors are considered to be one of the most promising energy storing devices. Nowadays SCs are attracting more attention, because of them embracing great potential for a wide range of applications [8].

The supercapacitors, also known as Electrochemical capacitors, store energy with an electric double-layer capacitance achieved by ion adsorption or pseudocapacitance dominated by a surface redox reaction. Pseudocapacitors with conducting polymers or metal oxides as electrode material, although demonstrating high capacitive performance, but cannot maintain this performance after prolonged cycling. On the other hand, Electric double-layer capacitor (EDLC) can be charged and discharged as many as one million cycles without performance degradation [9]. However, they suffer from a low gravimetric capacitance and gravimetric energy density as the charge is stored only at the electrode-electrolyte interfaces. Currently, modern-day electrical and electronic devices demand high current, energy, and power requirements with extreme safety and precautions. Supercapacitors are one of the solutions to meet these tremendous requirements of high power density, emitting a large amount of energy in a short time period. At ideal conditions, supercapacitors can replace batteries satisfying power requirements in electric vehicle systems combining both high power density of supercapacitors and high energy density of batteries. When in need of rapid acceleration, supercapacitors can dispense large amounts of power batteries could help in electrically charging the capacitors and to power the vehicle [10]. Based on these key characteristics, comprehensive efforts have been made by the researcher's development of advanced materials and the rational assembly of SCs to meet energy needs.

Electrodes, as key components, play a significant role in determining the overall performance of SCs. At various electrodes, thin-film electrodes (TFEs) represent a smart type and are made up of layers of active material with a thickness ranging from nanometers to hundreds of micrometers. In particular, there are TFEs rapid electrochemical responses are due to their short charge and ion transport distance. Furthermore, TFEs exhibit advantages in the assembly of high-performance devices that are easy to integrate with portable electronics [11, 12]. TFEs with greater thicknesses are desirable to provide a larger areal energy density. Since the charge storage in TFEs involves processes at the interface between the electrolyte and the active substance, it is essential to ensure that the electrolyte which has as much access to the surface active part. Therefore, having TFEs greater thicknesses

(typically > 20 nm) tosses hierarchical pores that provide channels for efficient electrolyte penetration [13]. Recently, an investigation into free-standing TFEs was also conducted. These TFEs are useful for improving the performance of the device by avoiding the use of active current collectors, as these electrodes must have exceptionally high conductivity and good mechanical strength. Free-standing TFEs are commonly used to create flexible solid-state SCs.

2. LITERATURE SURVEY

The search for high-performance supercapacitive materials that can deliver as high energy density as conventional capacitors and conventional batteries has never landed among the research community. Among various electrode materials, transition metal chalcogenides have attracted significant attention due to their intricate electrochemical properties such as rich redox chemistry, high valence levels, high electronic conductivity compared to their oxide counterparts, fast ion diffusion kinetics and morphological diversity; However, they are prone to poor rate performance, cyclability, surface area, and agglomeration issues.

Tang *et al.,* [13] prepared Cu_2ZnSnS_4(CZTS)/reduced graphene oxide composite by a hydrothermal treatment of the mixture of CZTS and graphene oxide (GO) and achieved maximum specific capacitance of 591 F g^{-1} at a current density of 0.25 A g^{-1} with excellent capacitance retention of 80.6 % after 1000 GCD cycles. Sahoo *et al.,* [14] synthesized a series of isostructural Cu_2MSnS_4 (M= Fe, Co, Ni) compounds by simple crystallization coupled with reflux method and examined the cation distribution and its effect on the pseudocapacitive behaviour of Cu_2MSnS_4 electrode. Cu_2NiSnS_4 on Ni-foam exhibited highest specific capacitance of 1425 F g^{-1} at a current load of 1 A g^{-1} and exhibits superior cyclic lifespan with 77 % retention of the initial capacitance over 4000 cycles.

Sarkar *et al.,* [15] reported the synthesis of flowerlike Cu_2NiSnS_4 microspheres by a simple hydrothermal method. Further utilized the same as positive electrodes for solid state asymmetric supercapacitors, which demonstrated a high specific capacitance of 1639 F g^{-1} at a scan rate of 5 mV s^{-1}. The device attains a maximum energy density of 30.88 Wh Kg^{-1} with high power density of 2.42 kW Kg^{-1}, and superior capacitance retention of the device is reflected by maintaining 95.7 % of initial capacitance after 2000 cycle run. Marigold flower like structured Cu_2NiSnS_4 nanoparticle was prepared by Isacfranklin *et al.,* [16] through hydrothermal method

and examined it electrochemical properties. Thus prepared electrode revealed high specific capacitance about 1029 F g^{-1} at current density 0.5 A g^{-1}. Further, it retained 78.65 % capacity over 5000 cycles. To prove the practical applicability, a full-cell asymmetric solid-state device was fabricated and delivered energy density was 41.25 Wh Kg^{-1} and power density was 750 Wh Kg^{-1}.

The Cu_2FeSnS_4/PVP/rGO-decorated nanocomposite using PVP as the surface ligand was explored in a simple one-step solvothermal route, the full cell three-electrode arrangements delivered 748 C g^{-1} at 5 mV s^{-1} employing CV and 328 F g^{-1} at 0.5 A g^{-1} employing GCD respectively [17].

3. OBJECTIVES OF THE PRESENT STUDIES

Based on the earlier report, this perspective thesis work focused on Successive ionic layer adsorption and reaction method (SILAR) deposited nanostructured quaternary thin film electrodes for supercapacitor (Electrochemical capacitors) application. The main objectives of this work include:

- To prepare novel nanocrystalline quaternary Cu_2XSnS_4 (X= Zn, Co and Ni) thin films electrodes by SILAR method

- To characterize the prepared films using XRD, SEM-EDS, AFM and UV-visible techniques for the determination of structural, surface morphological, compositional, topographical and optical properties, respectively.

- The optimized thin film electrodes are subject to electrochemical studies such as cyclic voltammetry, charge-discharge and electrochemical impedance spectroscopy.

4. RESEARCH PROBLEM

The development of flexible and portable electronics requires thin flexible and wearable energy storage devices that serve both high power and energy densities with their high durability and flexibility. Thus, extensive work is devoted to a wide variety of flexible, stretchable and portable rechargeable supercapacitors and batteries [18]. Numerous improvements have been made to the material design with the thin film electrode and the flexible device structure and their electrochemical performance.

From scaling, the development of micro electrochemical power sources with thin film configuration design opens the door to operating modest devices such as electronic chip units, biomedical compatible devices and credit card/debit cards and personal sensor systems. Thin film technology is useful for understanding the essential properties of electrolyte-active materials in energy storage systems such as supercapacitors with polymeric binder and lithium-ion batteries (cathodes, anodes and solid electrolytes) without carbonaceous preservatives [19]. Here we explain why the thin film energy saving device is an important need of the society as it mainly depends on certain specific features like morphology, size, thickness, aperture size in the form of thin film energy storage.

In order to produce compact devices, aggregate integration of active electrode materials may not be an appropriate cause for problems. These demands for thin film products that facilitate expansion of compact devices and bind significantly less to electrode fabrications. The bulk SCs have two major drawbacks, which limit their application to electrical and electronic equipment suitable for transport. Initially, device manufacturing involved high-cost packaging materials and device preparation techniques to avoid possible leakage of electrolytes, as most organic electrolytes were highly toxic and corrosive. Furthermore, it is challenging to create small and flexible thin SC devices using the liquid electrolytes that cause the packaging problem.

5. ORGANIZATION OF THESIS

The thesis is composed of seven chapters, organized as follows.

Chapter I: Introduction

The chapter one describes the overview about the major global issue on energy demand and the importance of finding alternative resources, development of advanced energy storage devices like supercapacitor, challenges of supercapacitor and the role of electrode materials in supercapacitor application. Also gives an elaborate introduction to thin films and the basic mechanisms of film deposition and various deposition techniques are discussed

Chapter II: Literature Review

In chapter two discus about details of material under study, the literature survey of the quaternary films for supercapacitor application. The selection of CXTS electrode materials with rational nanostructured designs has resulted in improved electrochemical properties for high performance and has reduced the cost of SCs. In this chapter, mainly spotlight the metal chalcogenide based nanostructured electrode materials for electrochemical SCs. Finally, the scope of the thesis was described

Chapter III: Characterization techniques

This chapter elucidated a brief explanation on the primary principles of the characterization techniques. It is decided to investigate the nanocrystalline structure, optical, morphological, compositional and electrochemical features of the deposited thin films using XRD, FTIR, UV visible, AFM, SEM-EDS and electrochemical studies such as cyclic voltammetry (CV), chronopotentiometry (GCD) and electrochemical impedance spectroscopy (EIS) with cycling stability analyses.

Chapter IV: Preparation and Characterization of Cu_2ZnSnS_4 thin film electrodes

This chapter deals the preparation and optimization of CZTS thin film electrodes with SILAR deposition. The Schematic representation of preparation for thin films by SILAR method is shown Figure 1. The following are the parameters that influence the film properties.

- Number of dipping cycle
- Adsorption and reaction time
- Concentration of Zn in CZTS

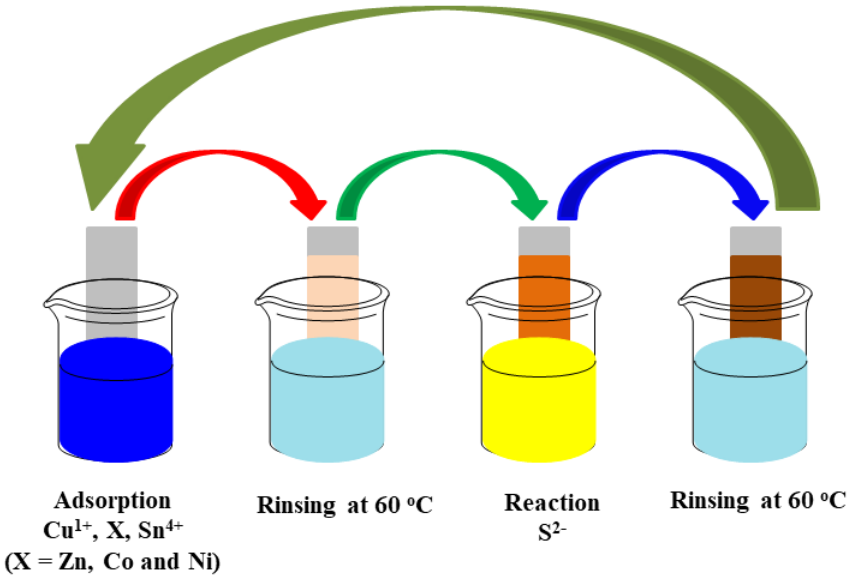

Figure 1 Schematic representation of preparation of thin films by SILAR method

Number of dipping cycle

The Cu_2ZnSnS_4 thin films have been successfully deposited on a glass substrate prepared by SILAR method. The XRD patterns were matched with both wurtzite and kersterite phase CZTS, which is in good agreement with the earlier reports in the literature. The surface morphology for all annealed CZTS thin films observed using SEM shows relatively uniform, densely packed surface and the presence of spherical like particles, EDS spectra taken for CZTS films confirm the presence of expected Cu, Zn, Sn and S elements. The optical energy band gap for the annealed films CZTS-80 and CZTS-100 are 1.57 and 1.51 eV respectively, which are in close agreement with the reviewed literature value. The optimized films have been examined for their electrochemical performance such as cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy measurements in 1 M KOH electrolyte solutions. It is found that the nickel foil electrode reveals a maximum specific capacitance of 156 F g^{-1} at a current density of 1 A g^{-1}. These electrochemical studies suggest that the prepared CZTS film electrode is considered to be one of the positive electrode materials for supercapacitor applications.

Adsorption and reaction time

In this research work, CZTS thin film electrodes prepared based on various adsorption and reaction times of cation and anion. The XRD patterns were well matched with mingle phase of wurtzite and kesterite phase with the tetragonal structure of CZTS. The surface morphology for the annealed films shows relatively uniform, densely packed surface and agglomerated spherical like particles, expected Cu, Zn, Sn and S elements present in the films were identified by EDS spectra. In AFM analysis spherical like particles were observed and the maximum number of particle size is obtained 171 nm. UV–vis spectra were good absorption in the entire visible range, calculated optical energy band gap of 1.46–1.82 eV. The Cyclic voltammetry curve of CZTS-52 film electrode at different scan rate (Figure 2). The CV and GCD results show psudocapacitance nature of the electrode material with a maximum specific capacitance of 182.54 F g^{-1} at a current density of 1 A g^{-1}. After operation of continuous 1000-time charge-discharge cycles the electrode retains about 61.92 % of its initial capacitance. The working electrode also exhibits the maximum power density of 941.17 W Kg^{-1} and maximum energy density of 4.05 Wh Kg^{-1}.

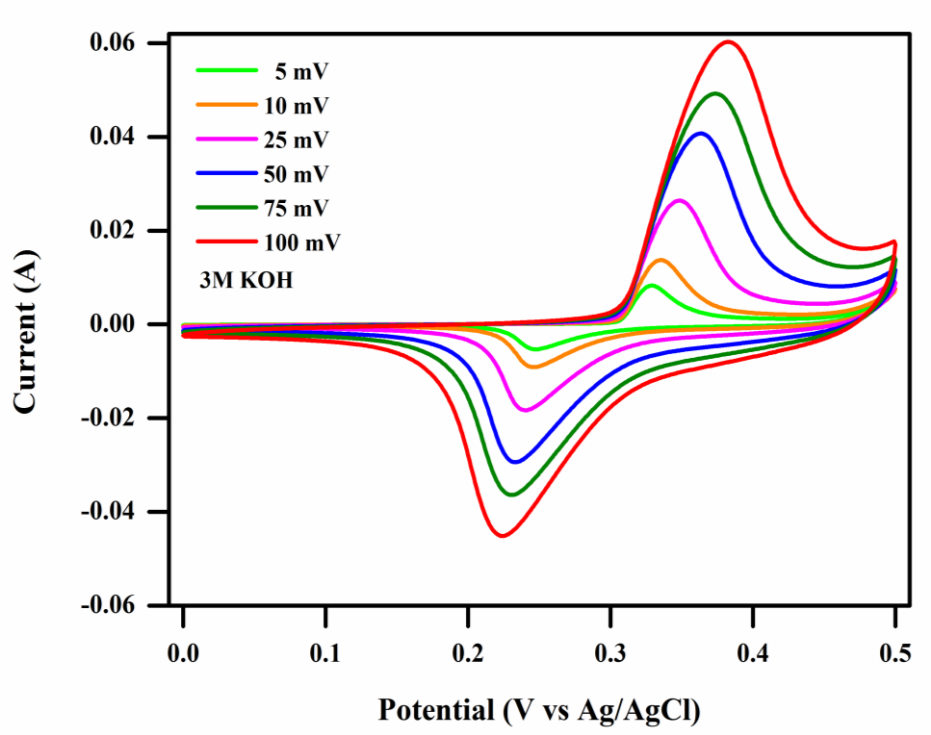

Figure 2 Cyclic voltammetry curve of CZTS-52 film electrode.

Concentration of Zn in CZTS film

The effect of zinc concentrations (0.05–0.2 M) on nanoscale CZTS films properties was investigated. An increase in zinc concentration improves the crystallinity of Cu_2ZnSnS_4 films with emerging the preferential orientation along (200) and (100) lattice plane and confirmed the presence of the mingled wurtzite and kesterite phase. The prepared Cu_2ZnSnS_4 films of Z3 and Z4 have band gaps slightly outside the ideal range of Cu_2ZnSnS_4 films due to the increase in film thickness. The electrochemical measurement showed that the specific capacitance for Cu_2ZnSnS_4-Z2 in 3 M KOH aqueous electrolyte is as high as 165.04 F g^{-1} at a current density of 1 Ag^{-1}. GCD curve of CZTS-Z2 film electrode and at a constant discharge (Figure 3) current density of 3 Ag^{-1}, 96.5% of the initial capacitance still remained after 1000 cycles, indicating that the Cu_2ZnSnS_4-Z2 showed a good cycling stability.

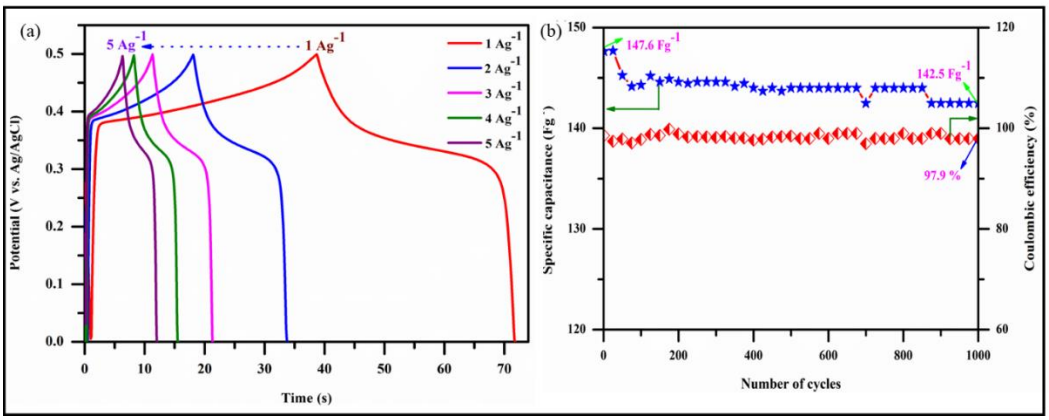

Figure 3 (a) Charge-discharge curve of CZTS-Z2 at different current densities and (b) at a constant charge/discharge at current density of 3 Ag^{-1}

Chapter V: Preparation and Characterization of Cu_2CoSnS_4 thin film electrodes

Chapter five describes the preparation and Characterization of Cu_2CoSnS_4 (CCTS) thin film electrode. Nanoscale quaternary chalcogenide Cu_2CoSnS_4 thin film electrode was deposited by SILAR method and used as a potential candidate in supercapacitor application. The XRD analysis revealed that Cu_2CoSnS_4 thin films have a typical tetragonal structure and Space group is $I\bar{4}2m$ in a preferred orientation along the direction (112). The remarkable electrochemical performances have been exhibited. The active materials of Cu_2CoSnS_4 thin film revealed an excellent specific capacity of 259.71 F g^{-1} at 1 A g^{-1} in GCD and retained 91.45 % capacity after 1000 cycles. It exhibits 10.91 W h kg^{-1} energy and 1527.77 W kg^{-1} power densities.

Chapter VI: Preparation and Characterization of Cu_2NiSnS_4 thin film electrodes

In this chapter the spherical like surface morphology Cu_2NiSnS_4 (CNTS) thin film were successfully deposited by simple and cost effective SILAR method. The XRD analysis revealed that CNTS thin films have a typical cubic structure in a preferred orientation along the direction (111). Detailed electrochemical analysis demonstrate that the electrode material possess high specific capacitance with good cycle stability. The as prepared thin film electrode had achieves high specific capacitance values is 1115.32 F g^{-1} at applied current density is 1.5 mA. It can deliver a maximum energy density of 13.94 Wh Kg^{-1} and power density is 833.3 W Kg^{-1}. The GCD, EIS and Ragone plot spectra of CNTS electrode is given in Figure 4. After operation of continuous 1000-time charge-discharge cycles the electrode retains about 95.37 % of its initial capacitance.

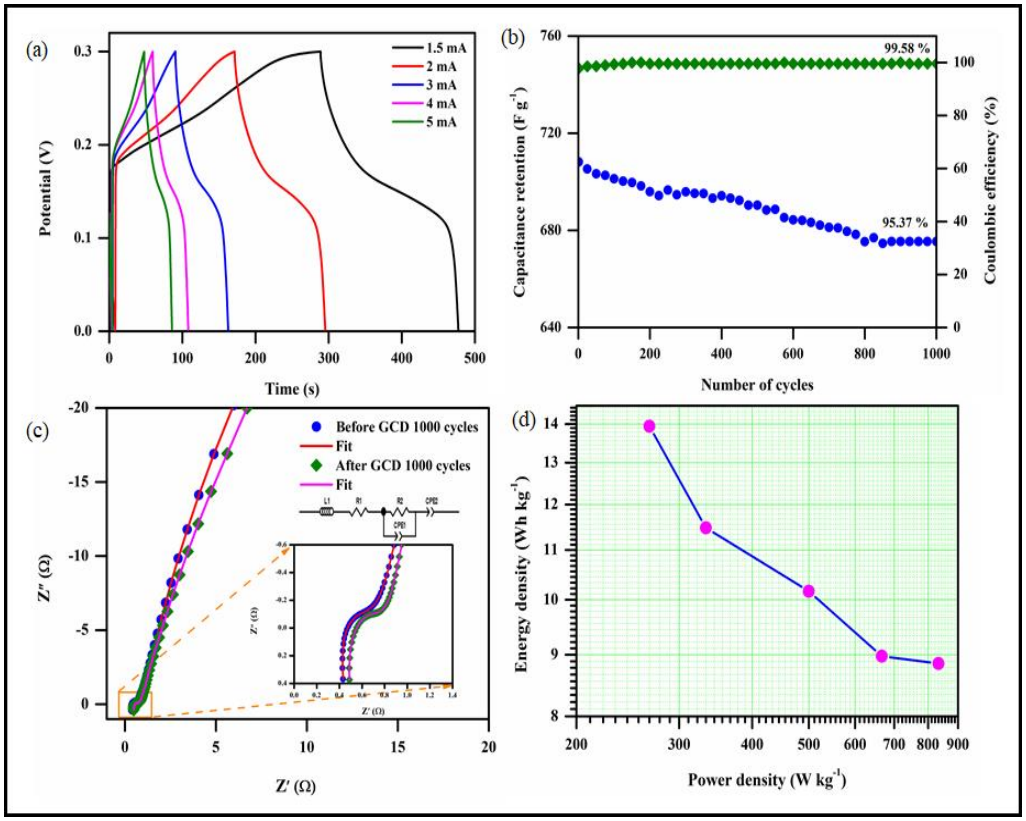

Figure 4 (a) GCD profile (b) GCD analysis of continuous charge/discharge of 1000 cycles (c) EIS of CNTS thin film electrode (Figure inset shows equivalent circuit) and (d) Ragone plot

Chapter VII: Summary and Future Work

This chapter summarizes the overall results and recommends the possible ways to improve the present studies for future research in this field. The Table 1 shows are summary results of the electrochemical behavioral studies of all prepared thin film electrodes.

Table 1 Summary of electrochemical parameters of thin film electrodes

Thin film electrode	**C_{sp} (F g^{-1})**		**P (Wkg^{-1})**	**E ($Wh\ kg^{-1}$)**	**Retentivity (%)**	**Columbic Efficiency (%)**
	CV (5 mV s^{-1})	**GCD (1 A g^{-1})**				
CZTS-100	416.12	154.11	3041.66	4.38	92.86	97.52
CZTS-52	407.65	128.75	941.17	4.05	61.92	99.19
CZTS-Z2	367.80	155.73	3124.99	5.73	96.50	97.91
CCTS	691.99	250.70	1527.77	10.91	91.45	99.63
CNTS	1678.23	917.93	833.33	13.94	95.37	99.58

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7. LIST OF PUBLICATIONS

1. **A. Murugan,** V. Siva, A. Shameem, and S. Asath Bahadur, Effect of Zn on nanoscale quaternary Cu_2ZnSnS_4 thin film electrodes for high performance supercapacitors, *Journal of Energy Storage*, **44** (2021), 103423.
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